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Organochlorine micropollutants in the Jiulong River Estuary and Western Xiamen Sea, China

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Abstract

Organochlorine contaminants including 12 polychlorinated biphenyl (PCB) congeners and 18 insecticides were determined in water, pore water and sediments of the Jiulong River Estuary and Western Xiamen Sea, China. The results showed that the levels of the total PCBs ranged from non-detectable to 1500 ng l^{-1} in water, from 209 to 3870 ng l^{-1} in pore water, and from 2.78 to 14.8 ng g^{-1} dry weight in sediments. Total organochlorine insecticide concentrations were from below the limit of detection to 2480 ng l^{-1} in water, from 267 to 33400 ng l^{-1} in pore water, and from 4.22 to 46.3 ng g^{-1} dry weight in sediments. Concentrations of PCBs and insecticides in pore water were significantly higher than those in surface water, due to the high affinity of these hydrophobic compounds for sediment phase. The PCB congeners with the highest concentrations were CB153, CB180 and CB194, which together accounted for 68–87% of total PCBs in water, pore water and sediment. Among the hexachlorocyclohexane (HCH) compounds, beta-HCH was found to be a major isomer. Analysis of 1,1,1-trichloro-2,2-bis-chlorophenyl-ethane (DDT) and its metabolites showed that 1,1-dichloro-2[*o*-chlorophenyl]-2[*p*-chlorophenyl]-ethylene (DDE) was dominant in the group. In comparison to a 1998 study in the Western Xiamen Sea, levels of organochlorines were enhanced due probably to recent inputs and changes in sediments.

Keywords: Organochlorine insecticides; DDT; Lindane; PCBs; Jiulong River Estuary; Western Xiamen Sea

1. Introduction

Among a large number of man-made chemicals, organochlorines such as 1,1,1-trichloro-2,2-bis-chlorophenyl-ethane (DDT), polychlorinated biphenyls (PCBs) and hexachlorocyclohexanes (HCHs) are of great concern due to their highly persistent nature and global occurrence (Glynn et al., 1995; Tkalin, 1996). These chemicals are bioaccumulative in nature, can biomagnify in the food web and induce various toxic effects in marine mammals (Pridmore et al., 1992; Klamer and Fomsgaard, 1993). In addition, they can cause the so-called endocrine disruption (ED) effects, by inducing abnormal thyroid function in Herring gull, feminisation in Western gull, and can impair Avian reproduction, among other deleterious effects (Carmichael, 1998). Even after being banned, organochlorines such as DDT and lindane are still being produced and used in many countries in agriculture and for the control of diseases such as malaria and typhus (Pham et al., 1996; Tkalin, 1996; Wu et al., 1999; Nhan et al., 2001).

Jiulong River Estuary is one of the largest river/estuary systems in South China, with a length of 285 km and an area of 14741 km^2. It is the major source of

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freshwater to Xiamen coastal seas. The estuary is characterised by intense agricultural activities and rapid industrial development, and represents a potential major source of pollutants in Xiamen coastal waters. The rapid development of the Xiamen Economic Special Zone since 1986 has resulted in significant stress to Xiamen Harbour and its surrounding environments. Hong et al. (1995) showed that organic pollution in Xiamen waters has increased steadily in recent years, and that there was a significant petroleum and organochlorine contamination in Xiamen Harbour sediments. More recent studies by Zhou et al. (2000) and Maskaoui et al. (2002) also found these contaminants in water, pore water and sediments in Xiamen Harbour. However, up to today, little data is available on the levels of chlorinated contaminants in the Jiulong River Estuary, yet it can be a major source of pollution to Western Xiamen Sea. Chlorinated contaminants may be present in the dissolved phase or associated with sediment, both of which may be available for bioaccumulation. The interactions between dissolved pollutants and particles (inorganic and organic) and the degradation of pollutants will determine their fates and bioavailability in aquatic systems. This project aims to fill gap in our knowledge, by assessing the levels of selected organochlorine micropollutants in the Jiulong River Estuary as well as Western Xiamen Sea in an integrated approach, focusing on the main phases in which pollutants may accumulate including water, sediment and sediment pore water.

2. Materials and methods

2.1. Chemicals

Reference PCBs (12 congeners, each at $10\,\mu g\,ml^{-1}$) and insecticides (18 compounds, each at $2000\,\mu g\,ml^{-1}$) were obtained from Supelco. Working standard of insecticides was prepared by diluting the stock solution in cyclohexane. PCB stock was used directly. These were further diluted with cyclohexane to prepare calibration solutions for cGC analyses in the range $0.01–2\,ng\,\mu l^{-1}$. All solvents used for sample processing and analyses including dichloromethane (DCM), ethyl acetate, acetone, hexane, cyclohexane and methanol were of analytical grade and further distilled twice to remove impurities. Deionised water was taken from a Milli-Q system (Millipore, Watford).

2.2. Sampling and sample treatment

Subsurface (0.5 m) water samples from Jiulong River Estuary and Western Xiamen Sea were collected from aboard a chartered vessel, during axial surveys in June 1999. The locations of the sampling stations are shown in Fig. 1. Throughout the survey a global positioning system was used to locate the sampling positions, and a conductivity, temperature and depth sensor was deployed for obtaining these master variables. Samples were taken using pre-cleaned glass bottles, which were thoroughly washed with detergents, Milli-Q water and DCM, and dried before use. Aliquots of the sample (1.0 l) were filtered under vacuum through pre-ashed glass fibre filters (Whatman, GF/F) to obtain dissolved samples. Additional water samples were also filtered and acidified to obtain samples for dissolved organic carbon (DOC) analysis using a Shimadzu 5000A total organic carbon analyser. The data for the major physicochemical parameters is shown in Table 1.

Surface sediment samples were collected with a grab sampler, and the top 1-cm surface layer was carefully removed with a stainless steel spoon and stored in pre-ashed glass bottles. After returning to the laboratory, the sediments were centrifuged (3000 rpm) at 4 °C to

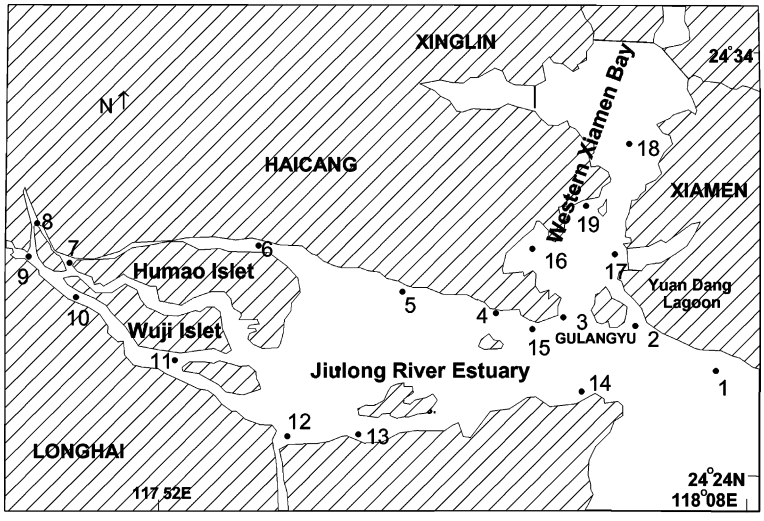

Fig. 1. Map of sampling stations in the Jiulong River Estuary and Western Xiamen Sea, China.

Table 1
Summary of conditions when water and sediment samples were taken in the Jiulong River Estuary and Western Xiamen Sea, China

Station	Depth (m)	Current speed ($cm\,s^{-1}$)	Temperature (°C)	Turbidity (FNU)	Salinity (‰)	DOC (μM C)
1	1	40	28.94	4.95	24.58	880
	6	34	28.94	5.90	27.13	
2	1	59	27.52	18.29	31.00	993
	5	43	27.49	16.16	31.00	
3	1	20	27.73	7.48	31.20	437
	5	51	27.66	8.48	31.50	
4	1	0	28.55	4.84	26.00	467
	5	19	27.66	23.07	31.40	
5	1	6	28.80	9.26	21.80	707
	4	6	27.97	23.07	29.10	
6	1	26	29.01	11.23	5.08	1175
	5	23	28.83	17.15	9.11	
7	1	43	29.98	23.13	0.10	1258
	3	13	29.60	23.13	0.10	
8	1	59	30.37	12.92	0.10	1370
	4	13	29.01	14.07	0.10	
9	1	41	30.02	16.43	0.10	
	3	49	29.91	16.87	0.10	
10	1	41	30.02	23.16	0.13	1146
	5	49	29.91	23.13	0.13	
11	1	21	29.88	23.13	0.13	2091
	4	11	29.81	23.10	0.13	
12	1	17	29.60	23.10	0.13	1368
	4	120	29.84	23.10	0.16	
13	1	15	30.16	23.13	0.67	1338
14	1	75	28.97	23.07	15.45	1852
	4	62	28.97	23.07	15.96	
15	1	47	29.70	10.26	28.30	907
	5	30	29.60	9.12	28.60	
16	1	34	29.74	10.26	28.30	1323
	5	27	29.42	9.12	28.60	
17	1	7	29.28	16.63	28.30	533
18	1	28	29.56	5.00	27.20	897
	5	37	28.45	7.72	28.10	
19	1	10	29.49	4.10	26.90	1267
	5	22	29.77	11.99	27.80	

obtain sediment pore water. The centrifuged sediments were then stored at −20 °C till extraction.

2.3. Sample extraction for organochlorine compounds

Filtered water and pore water samples were extracted using a solid-phase extraction (SPE) system from Supelco, following established procedures (Zhou et al., 1996, 2000). The Supelco SPE cartridges were first washed with 5 ml of ethyl acetate, then conditioned with 5 ml of methanol followed by $2 - x5$ ml of Milli-Q water. Water and pore water samples were passed through the cartridges at a flow rate of $6\,ml\,min^{-1}$ under vacuum. Following extraction, the cartridges were eluted with 3 ml of ethyl acetate, which was combined with an ethyl acetate rinse (10 ml) from the extraction glassware. After water was removed from the extracts by ashed Na_2SO_4, the extracts were reduced in volume by N_2 blow-down in a water bath.

Sediment samples were extracted by ultrasonication. All glassware was thoroughly washed with detergent, Milli-Q water and DCM, and ashed in a muffle furnace. Sediment samples (approximately 30 g wet weight) were mixed with freshly prepared Cu granules and ashed Na_2SO_4, and then extracted twice in 100-ml mixture of

hexane and DCM (1:1) for 30 min. The extracts were concentrated to 0.5 ml by rotary-evaporation and under a gentle stream of nitrogen. The concentrated extracts were purified by passing through silica gel, followed by elution with DCM (3.5 ml) to obtain PCBs and organochlorine insecticides (Hong et al., 1995; Zhou et al., 2000). All the extracts were concentrated by gentle N_2 blow-down to about 100 µl.

2.4. Analyses

A Hewlett-Packard 5890 GC with an electron capture detector (ECD), an autosampler, and Chemstation software was used for determining the levels of PCBs and organochlorines in water and sediment samples. The capillary column used for the analyses was a BPX-5 (Hewlett Packard HP-5 equivalent, 45 m × 0.22 mm i.d. × 0.25 µm film thickness). The oven temperature for analyses was programmed from 60 °C (initial time, 1 min) to 140 °C at a rate of 20 °C min^{-1}, 140–236 °C at a rate of 3 °C min^{-1}, 236–290 °C at 4 °C min^{-1} and held at 290 °C for 1 min.

Before analysis, relevant standards were run to check column performance, peak height and resolution, and the limits of detection (LoD). With each set of samples to be analysed, a solvent blank, a standard mixture and a procedural blank were run in sequence to check for contamination, peak identification and quantification. Compounds were identified mainly by their retention times. Selected samples were analysed by GC/MS for confirmation. All results for sediment samples were reported on a dry-weight basis.

2.5. Quality assurance

All analytical data are subject to strict quality control procedures. As no standard reference material for organochlorines in seawater is currently available, procedural blanks and spiked samples were analysed with each set of samples. Spiked water and sediment samples were determined with good precision, from 64 ± 9% to 96 ± 4% for water samples, and from 60 ± 6% to 96 ± 9% for sediment samples (Zhou et al., 2000). In addition, the errors involved in sampling were assessed by carrying out triplicate sampling of water at the same site and the analysis of sample extracts. Results (Zhou et al., 2000) showed good reproducibility of the whole procedure.

3. Results and discussion

3.1. PCBs

In subsurface water, total PCBs varied from below the limit of detection (<0.1 ng l^{-1}) at Stations 12 and 13 to 1500 ng l^{-1} at Station 8 (Fig. 2), with a mean value of 355 ng l^{-1}. The highest PCB concentration was found at the river end of the estuary (Station 8). High concentrations (around 500 ng l^{-1}) were also found at Stations 5, 6 and 10. The levels of total PCBs in Western Xiamen Sea were higher than those found in 1998 (Zhou et al., 2000). This suggests some recent inputs of these contaminants especially near Dongdu Port and the mouth of Lake Yuandang (Stations 17, 18 and 19). The PCBs

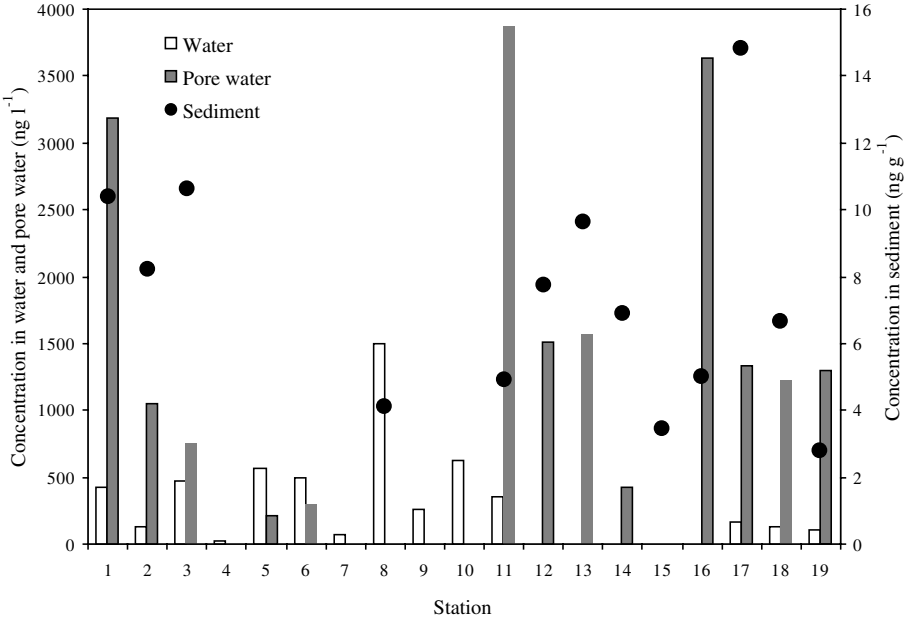

Fig. 2. Concentration distributions of total PCBs between water, pore water and sediments at different stations in the Jiulong River Estuary and Western Xiamen Sea, China.

could come from the direct discharges from a power plant and a painting factory in Haicang, and the continuing use of PCB-containing capacitors and transformers. Other important sources of PCBs in the area may include volatilisation from previously contaminated soils, followed by atmospheric transport and deposition (Galassi et al., 1992; Kallenborn et al., 1998). In a coastal environment such as Western Xiamen Sea surrounded by intensive agricultural activities and a diverse range of industry, with many different sources of PCB inputs, both point and diffuse, it is difficult to identify a clear source–occurrence relationship. Furthermore, the sediment resuspension from tidal movement in the estuary may promote chlorination dependent differential transport further masking source–concentration matches (Tyler and Millward, 1996).

In comparison, the levels found in this study are higher than those in UK estuarine waters (Zhou et al., 1996), and those in Midway Atoll (North Pacific Ocean) where PCBs ranged from 9.1 to 63.0 $ng\,l^{-1}$, with a mean value of 24.0 $ng\,l^{-1}$ (Hope et al., 1997). Therefore water in Jiulong River Estuary and Western Xiamen Sea was polluted by PCBs.

The total PCB concentration in pore waters ranged from 210 $ng\,l^{-1}$ at Station 5 to 3870 $ng\,l^{-1}$ at Station 11, with a mean concentration of 1570 $ng\,l^{-1}$ (Fig. 2). The levels are higher than those detected in a 1998 study, suggesting either that there have been recent inputs of PCBs in the region and/or that there may have been significant changes in the sediments (e.g. sediment dynamics, sediment properties). In comparison to the 1998 study, samples in 1999 were taken after a major typhoon; it is therefore probable that sediments in the area had been resuspended and reworked prior to sampling. Such sediment resuspension and mixing would result in the surfacing of contaminated sediments and release of previously adsorbed PCBs from sediment to water, and lead to changes in the distribution and partition of PCBs between water, sediment and pore water. High concentrations of total PCBs were also found at Station 16 (3630 $ng\,l^{-1}$) in the Western Sea and at Station 1 (3180 $ng\,l^{-1}$) out of the Western Sea. It is clear that at all except two stations, the total PCB concentrations in pore water were 1–4 orders of magnitude higher than those in surface water, similar to the findings by Zhou et al. (2000). Such concentration difference between pore water and surface water may be due to the highly hydrophobic characteristics of PCBs and hence their strong tendency to become associated with organic colloids in sediments (Brownawell and Farrington, 1986). The significant difference between the concentration in water and pore water may induce a possible flux of PCBs from sediment to overlaying water.

Total PCBs level in sediment varied from 2.78 to 14.8 $ng\,g^{-1}$ dry weight in the area, with a mean value of 7.32 $ng\,g^{-1}$ (Fig. 2). The highest concentration was found inside the Western Sea at Station 17 (14.8 $ng\,g^{-1}$), which is located at the mouth of Lake Yuandang and hence receives a great deal of sewage discharges. Relatively high concentrations of PCBs (8.23–10.6 $ng\,g^{-1}$) were also found at the mouth of the Western Sea (Stations 1, 2 and 3), suggesting that sediments at these locations were more polluted by PCBs than at other sites. This may be due to the high tendency of these compounds to become associated with particles followed by sedimentation especially in the river mouth. In comparison to other regions, the levels were lower than those found in the new territories of Hong Kong where the total PCBs ranged from 43 to 461 $ng\,g^{-1}$ dry weight (Zhou et al., 1999), and lower than those detected in Pearl River Delta and Macao Harbour which were between 11.9 and 158 $ng\,g^{-1}$ (Fu et al., 1999). Similar levels of PCBs were also reported in other Chinese river/estuary systems (Wu et al., 1999), and in the Humber Estuary and plume (Klamer and Fomsgaard, 1993; Tyler and Millward, 1996).

In terms of individual congener distributions, most congeners were present in all water samples except at Stations 12 and 13 where no congener was detected, and at Station 16 where only three congeners were present. In both the water column and sediment, the congeners which made the largest individual contribution to total PCB concentrations were CB153, CB180 and CB194. The three compounds collectively accounted for 73%, 68% and 87% of total PCB concentrations in surface water, pore water and sediments, respectively. Less chlorinated congeners (CB101 and below) generally made up a small (<8%) individual contributions to total loading, except for CB52 which contributed to 17% in water and 22% in pore water. The observed finding of congener distribution towards more highly chlorinated compounds is consistent with previously published data indicating the preferential retention of these less volatile and more lipophilic compounds in the marine environment (Devoogt et al., 1990). Differences in congener composition in the aquatic systems may also be attributed to a decline in the proportion of less chlorinated PCBs that are more susceptible to losses through volatilisation, sedimentation, and possibly microbial degradation (Brown et al., 1987; MacDonald et al., 1992; Quensen et al., 1988). Moderately and higher chlorinated PCBs may therefore remain at relatively constant levels in the aquatic environment because they are less volatile, more soluble in lipids, adsorb more readily to sediments and are more resistant to microbial degradation (Connell, 1988; Shiu and Mackay, 1986; Tyler and Millward, 1996). Congener concentration in water and sediment may also be influenced by concentrations of PCBs in biota, suggesting that further study should focus on the bioaccumulation of PCBs in marine organisms in both Western Xiamen Sea and Jiulong River Estuary.

3.2. Organochlorine insecticides

As shown by Zhou et al. (2000), relatively low levels of organochlorine insecticides were found in Western Xiamen Sea in 1998. However, little data is available on the levels of such compounds in water and sediment of the Jiulong River Estuary, yet such information is essential for assessing the environmental quality of the estuary, for minimising any adverse effects to the aquatic organisms, and for preventing human risk from the consumption of seafood.

Total insecticides in water ranged from below the limit of detection to 2480 $ng l^{-1}$ at Station 8, with a mean value of 779 $ng l^{-1}$ (Table 2). High concentrations were also found at Stations 1, 3, 5, 10 and 11 (Fig. 3). The contamination profile indicates inputs from agricultural activities (e.g. via river runoffs). High insecticide levels were also observed at Station 17 (611 $ng l^{-1}$), close to a

Table 2
The concentration of organochlorine insecticides in water ($ng l^{-1}$), pore water ($ng l^{-1}$) and sediment ($ng g^{-1}$ dry weight) from the Jiulong River Estuary

Compounds	Water			Porewater			Sediment		
	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD
α-HCH	<0.1–23.5	3.5	7.2	0.3–471	74.3	146	<0.01–0.10	0.02	0.03
β-HCH	<0.1–99.6	39.9	32.4	23.1–15,400	1670	4160	0.34–0.1.00	0.60	0.16
γ-HCH	<0.1–7.8	2.1	2.3	0.4–24.7	11.5	15.2	0.01–0.03	0.02	0.01
δ-HCH	<0.1–249	26.1	59.4	7.8–1960	364	625	0.12–8.20	0.96	2.18
Heptachlor	<0.1–15.9	4.0	4.3	0.3–88.9	22.7	25.9	<0.01–0.07	0.02	0.02
Aldrin	<0.1–46.5	14.0	14.5	7.9–621	152	175	0.11–1.28	0.38	0.35
Heptachlor E	<0.1–4.3	0.76	1.4	0.2–82.2	12.4	24.4	<0.01–0.08	0.02	0.02
Endosulfan I	<0.1–7.6	1.46	2.1	0.4–59.1	21.8	16.1	0.01–0.26	0.04	0.07
4,4′-DDE	<0.1–40.9	11.6	14.4	0.5–129	18.4	34.8	0.01–0.40	0.07	0.12
Dieldrin	<0.1–278	55.1	84.5	12.7–888	248	308	<0.01–1.14	0.37	0.28
Endrin	<0.1–16.9	5.8	5.8	3.9–181	59.8	51.5	0.06–1.32	0.20	0.34
4,4′-DDD	<0.1–12.6	2.0	3.3	0.2–11.1	3.5	3.2	<0.01–0.05	0.01	0.01
Endosulfan II	<0.1–346	88.2	88.9	31.3–853	375	246	<0.01–3.92	1.32	0.94
4,4′-DDT	<0.1–9.7	1.2	2.8	0.2–52.9	9.2	16.0	<0.01–0.04	0.01	0.01
Endrin aldehyde	<0.1–456	203	145	18.6–9150	2440	2460	<0.01–16.60	2.69	4.71
Endosulfan sulphate	<0.1–737	208	212	74.9–2730	619	699	<0.01–10.40	3.75	2.37
Methoxychlor	<0.1–844	251	258	76.3–1460	341	367	1.25–3.13	1.94	0.59
Endrin ketone	<0.1–1.3	0.4	0.4	0.3–55.4	6.8	15.5	0.01–0.03	0.01	0.01
ΣHCHs	<0.1–352	71.1	85.5	31.6–17,400	2120	4660	0.48–9.00	1.59	2.25
ΣDDTs	<0.1–63.2	14.3	17.6	0.9–193	31.1	50.8	0.01–0.43	0.09	0.13
ΣPesticides	<0.1–2480	779	747	267–33,400	6450	8580	4.22–46.30	11.80	10.90

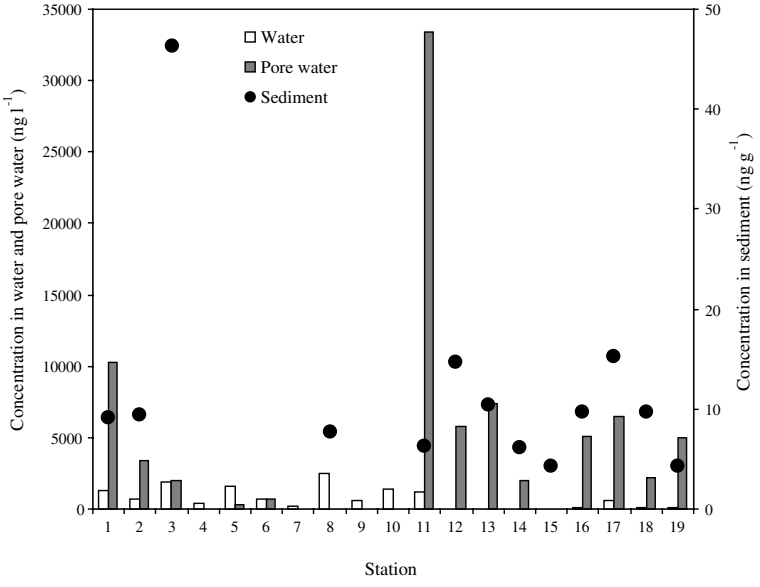

Fig. 3. Levels of total organochlorine insecticides in water, pore water and sediments at different stations in the Jiulong River Estuary and Western Xiamen Sea, China.

sewage outfall from Lake Yuandang. The results suggest that there are other sources of pesticide to Xiamen coastal waters, from for example, untreated sewage discharged from urban areas and from dumping of toxic industrial wastes from others locations in the Western Sea at Stations 16, 18 and 19 (51.3–65.3 $ng\,l^{-1}$). Currently on average 250,000 tons of agricultural chemicals a year are used in China, to help save 30 million tons of grain output and to prevent more than 400,000 tons of cottons and 8 million tons of vegetables from succumbing to pests, diseases and rodents (Zhao, 1999). The surprisingly low efficiency of agrochemicals (40% in many regions) means that some of them are wasted or find their way into water and soil, leading to pollution or sometimes to the death of animals. In comparison to a previous study (Zhou et al., 2000), the highest concentration in the present study was 2 orders of magnitude higher than in 1998, suggesting some recent inputs of organochlorines into the system being studied.

The levels of insecticides in pore water were from 267 to 33400 $ng\,l^{-1}$, with a similar spatial distribution character to PCBs in the area (Table 2). The highest concentration was detected at Station 11, which is located near the agricultural area of Longhai (Fig. 3). Relatively high concentrations were also found at Stations 1, 2, 12, 13, 16 and 17. Again, levels in pore water were significantly higher than those in surface water, implying a potential flux of insecticides to be transported from pore water to surface water. The higher levels in pore water than in surface water support our suggestion concerning the preference of hydrophobic compounds such as organochlorine insecticides for sedimentary environment than for water.

Total insecticides in sediments ranged from 4.22 to 46.3 $ng\,g^{-1}$ dry weight, with a mean level of 11.8 $ng\,g^{-1}$ (Fig. 3). Relatively high levels were found at the mouth of Jiulong River Estuary (Station 3, 46.3 $ng\,g^{-1}$), and at Stations 12 and 17 (14.7 and 15.3 $ng\,g^{-1}$). The mean concentration of organochlorine insecticides in sediment of Jiulong River Estuary and Western Xiamen Sea was similar to that (11.6 $ng\,g^{-1}$) found in Kingston Harbour sediments (Mansingh and Wilson, 1995), although was much lower than that observed in the sediments of Pearl River Delta and Macao Harbour, which was from 11.9 to 158 $ng\,g^{-1}$ (Fu et al., 1999). As to the individual insecticide, β-BHC, endrin aldehyde, endosulfan sulphate, methoxychlor and endosulfan II showed the highest concentrations in all the three phases. Together they made up 86% in water, 84% in pore water and 82% in sediments, respectively.

3.3. HCHs and DDTs

Table 2 shows that the total HCHs in water varied from below the limit of detection at Stations 12 and 13 to 352 $ng\,l^{-1}$ at Station 8, with a mean concentration of 71.1 $ng\,l^{-1}$. High levels (close to 100 $ng\,l^{-1}$) were also found in the mouth of the Jiulong River Estuary (Stations 1–5) and at Station 10. According to the Chinese seawater quality guideline (GB/3097-1997), in the grade 1 quality of seawater (which is considered to pose no hazard to marine ecosystem) the concentration of ΣHCHs should be lower than 1000 $ng\,l^{-1}$. So the quality of surface water of Jiulong River Estuary and Western Xiamen Sea is reasonably good as far as the level of ΣHCHs in water is concerned. Further analysis of HCH isomers shows that β-HCH was dominant in water samples (Fig. 4a), which on average represented 57% of total HCH concentrations in water. The results are consistent with previous findings by others (Zhou et al., 1996, 2000; Zhang et al., 2002), suggesting that β-isomer is highly resistant to degradation.

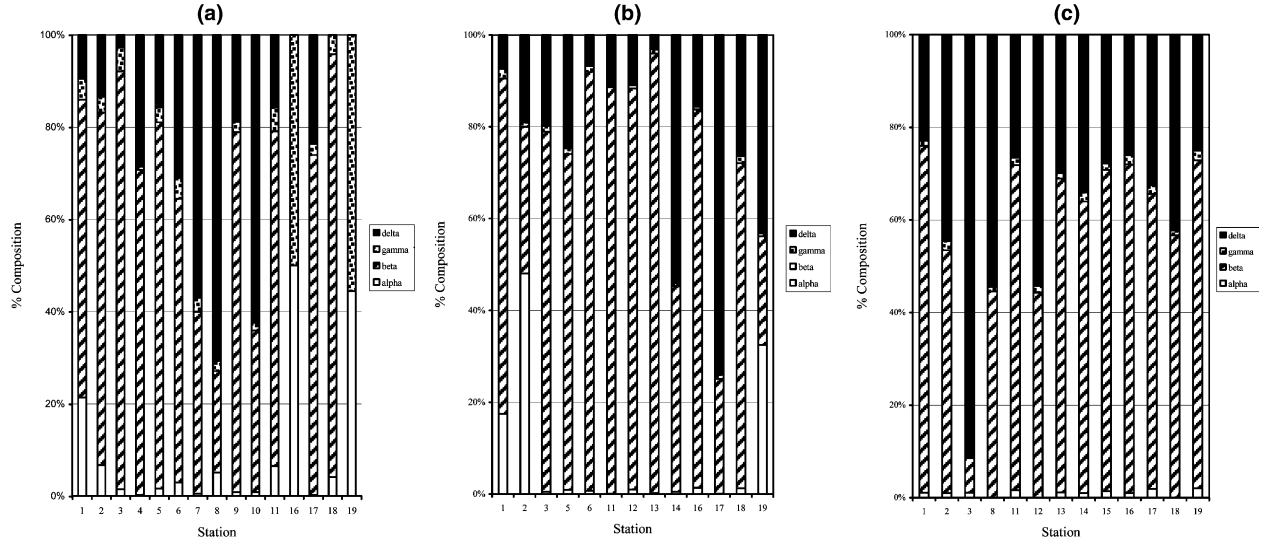

Fig. 4. HCH isomer distribution in (a) water, (b) pore water and (c) sediments.

The levels of ΣHCHs in pore water varied from 31.6 to 17400 $ng\,l^{-1}$, with the highest level found at Station 11, which is near the agricultural area of Longhai (Table 2). High levels (>1000 $ng\,l^{-1}$) were also found at Stations 1, 13 and 17. The ΣHCHs in sediments were in the range 0.48 to 9.00 $ng\,g^{-1}$, with the highest levels at the mouth of this estuary (Station 3). The levels were similar to those in sediments from the Japan Sea (Tkalin, 1996), from Viet Nam (Nhan et al., 2001), and from many other estuaries in China, but were 2 orders of magnitude lower than those in sediments from the Pearl River Estuary (Wu et al., 1999). Even lower levels ($\leqslant 0.07\,ng\,g^{-1}$) were reported for sediments from the Northern Florida Reef Tract (Glynn et al., 1995).

As to the individual HCHs, their mean concentration in water decreased in the order: β-HCH (39.9 $ng\,l^{-1}$) > δ-HCH (26.1 $ng\,l^{-1}$) ≫ α-HCH (3.5 $ng\,l^{-1}$) > γ-HCH (2.1 $ng\,l^{-1}$). The two isomers, β-HCH and δ-HCH, therefore made up 92% of total HCHs in water. A similar concentration order existed in pore water: β-HCH (1670 $ng\,l^{-1}$) ≫ δ-HCH (364 $ng\,l^{-1}$) ≫ α-HCH (74.3 $ng\,l^{-1}$) > γ-HCH (11.5 $ng\,l^{-1}$), and β-HCH contributed 66.6% to total HCHs in pore water (Fig. 4b). Again in sediments, the β-HCH accounted for 58.2% of total HCHs (Fig. 4c). Similar levels of individual HCHs were also found in surface sediments of the Baltic Sea, where the β-HCH was the major isomer, due to the fact that the β-isomer is more resistant to degradation (Dannenberger, 1996).

Total DDTs in water varied from 0.2 to 63.2 $ng\,l^{-1}$, with a mean value of 14.3 $ng\,l^{-1}$ (Table 2). Similar to the distribution of HCHs in water, the highest concentration was found at Station 8, and high levels were also found at Stations 1, 3, 6 and 9. Similar mean concentrations (0.30 to 3.02 $ng\,l^{-1}$) were also found in the raw water of the St. Lawrence River and its tributaries (Pham et al., 1996). According to the Chinese guideline (GB3097-1997), in the grade 1 seawater (which is considered to pose no hazard to the marine ecosystem) the concentration of ΣDDTs should be lower than 50 $ng\,l^{-1}$. So at one site of the Jiulong River Estuary, the ΣDDT level exceeded the guideline value, with a potential risk to the marine ecosystems. In pore water the levels of ΣDDTs ranged from 0.9 to 193 $ng\,l^{-1}$, with a mean value of 31.1 $ng\,l^{-1}$. The highest level was at the mouth of the estuary (Station 1). Relatively low concentrations of ΣDDTs were found in sediments, ranging from 0.01 to 0.43 $ng\,g^{-1}$. There are no guidelines on DDT levels in pore water and sediments, so no assessment can be made of the quality of the pore water and sediment under investigation. Similarly low levels of DDTs were also found in many other Chinese estuarine systems (Wu et al., 1999). However, higher levels of ΣDDTs were found elsewhere, for example, between 0.8 and 30.6 $ng\,g^{-1}$ in sediments from the Japan Sea, from 4.94 to 90.9 $ng\,g^{-1}$ in the sediments of Pearl River Delta (Fu et al., 1999), and from 7.40 to 80.55 $ng\,g^{-1}$ in sediments from Viet Nam (Nhan et al., 2001). Even higher concentrations (up to 30212 $ng\,g^{-1}$) were found in sediments along San Francisco Sea, California (Pereira et al., 1996).

As to the individual DDTs, the mean concentration in water decreased in the order: DDE (11.6 $ng\,l^{-1}$) > DDD (2.0 $ng\,l^{-1}$) > DDT (1.2 $ng\,l^{-1}$), and DDE occupied 69.9% of total DDTs in water (Fig. 5a). In pore water, DDE again dominated with the order: DDE (18.4 $ng\,l^{-1}$) > DDT (9.2 $ng\,l^{-1}$) > DDD (3.5 $ng\,l^{-1}$), and DDE contributed 53.9% to total DDTs in pore water (Fig. 5b). In sediments, a similar trend was observed: DDE (0.07 $ng\,l^{-1}$) > DDT (0.01 $ng\,l^{-1}$) = DDD (0.01 $ng\,l^{-1}$), and DDE accounted for 57.2% of total DDTs in sediments (Fig. 5c). The results therefore suggest that most of the DDTs in this area have been degraded to

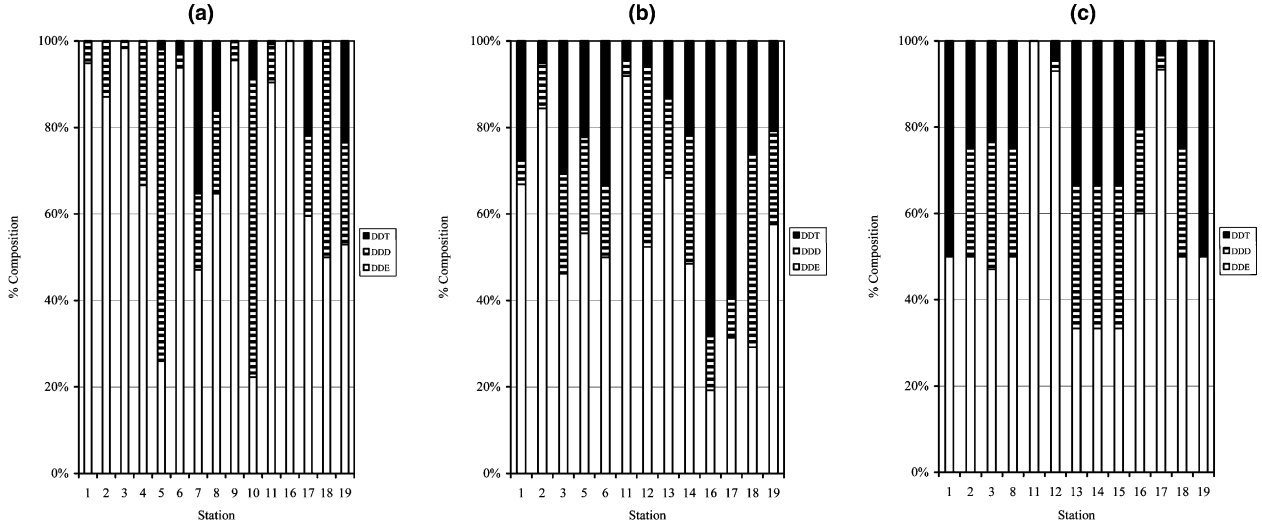

Fig. 5. DDT and its degradation products in (a) water, (b) pore water and (c) sediments.

form DDE and other metabolites through dehydrochlorination, and DDE is difficult to be degraded further (Pereira et al., 1996).

4. Conclusions

The distribution of selected PCBs and organochlorine insecticides in water, pore water and sediments in the Jiulong River Estuary and Western Xiamen Sea was studied. The levels of these contaminants in water were similar to those found in many other Chinese rivers/estuaries except the Pearl River Estuary where much higher concentrations were reported, but were higher than those found in other parts of the world (e.g. UK estuaries). The concentrations of contaminants in pore water were significantly higher than those in surface water, suggesting that such contaminants prefer to stay in a sedimentary rather than an aqueous environment. The concentration difference between pore water and surface water implies that potential fluxes can be set up in transporting micropollutants from sediments to overlying water. Relatively low levels of total PCBs and organochlorine insecticides were found in the sediments compared to other estuaries and coastal environments. In comparison to a survey in 1998, the contaminant concentrations were enhanced by 2 to 3 orders of magnitude, suggesting recent inputs of these chemicals into the system and/or substantial changes to the sedimentary environment from events such as typhoon.

In term of individual PCB congener distributions, highly chlorinated congeners such as CB152, CB180 and CB94 were the most abundant; together these three compounds accounted for 73%, 68% and 87% of total PCB concentrations in water, pore water and sediments, respectively. As to the concentration of individual insecticide, β-HCH, endrin aldehyde, endosulfan sulphate, methoxychlor and endosulfan II were the most significant; altogether they represented 86%, 84% and 82% of total organochlorine insecticides in water, pore water and sediment, respectively. Among the HCHs and DDTs, the compounds with the highest concentrations in all the three phases were β-HCH and DDE, suggesting that β-HCH is more resistant to degradation and that most of DDT has been transformed to DDE. The findings highlight that although chlorinated compounds such as PCBs and DDTs have been banned for use in China, they could still be detected in the environment, sometimes in high enough concentrations to cause toxicity. Due to the persistent nature of these compounds, urgent actions are needed to stop future use of any organochlorine-containing products (e.g. crop protection products, paints, transformers), by enforcing their collection and disposal. New legislation is required for the prosecution of illegal use of such products and better education of the public will also play a central role in the implementation of such measures.

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